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Notes

Structural Analysis of the e^2 and a^2 Isomers of $B_{20}H_{18}^{4-}$

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Introduction

We have previously reported that the reduction of $B_{20}H_{18}^{2-}$ with sodium in liquid ammonia[1,2] affords an isomer of $B_{20}H_{18}^{4-}$ formed as a product of kinetic control. On the basis of ^{11}B NMR spectra, the reduced complex was characterized[2] as two $B_{10}H_9^{2-}$ cages linked by a two-center equatorial–equatorial (e^2) B–B bond. Acidification and neutralization of e^2 resulted in its conversion to another isomer whose structural analysis by ^{11}B NMR indicated a complex in which the two $B_{10}H_9^{2-}$ cages were joined by a two-center apical–apical (a^2) B–B bond. We have now successfully confirmed the identities of the e^2 and a^2 isomers via single-crystal X-ray studies.

Experimental Section

Materials and General Procedures. All reagents were obtained from commercial sources and used without further purification unless otherwise noted. ^{11}B NMR spectra were recorded on a Bruker AM 500 (160.463 MHz) NMR spectrometer. The ^{11}B chemical shifts are referenced to external $BF_3 \cdot OEt_2$; peaks upfield of the reference are designated as negative and areas are given in parentheses. Infrared spectra were obtained from KBr pellets using a Beckman Model FT 1100 FT-IR.

Preparation of $K_4B_{20}H_{18}$ (K_4e^2).[2,3] The salt[4] $[Et_3NH]_2[B_{20}H_{18}]$ (2.0 g, 4.5 mmol) was dissolved in liquid ammonia maintained in a dry ice/acetone bath. Metallic sodium was added until the blue color persisted for approximately 5 min. After the ammonia was evaporated away, the residue was dissolved slowly in 50 mL of ethanol in an ice bath and a saturated solution of potassium acetate in ethanol was added to precipitate the product. After being washed with ethanol, the product was recrystallized in 76% yield from hot water and ethanol (1.5 g, 3.5 mmol). IR (KBr): 3600 (s), 2457 (s), 1607 (m), 1032 (s), 917 (m), 868 (m), 736 (m), 670 (m) cm^{-1}. ^{11}B NMR (H_2O): −29.51 (d, 6 B), −28.54 (d, 4 B), −27.15 (d, 4 B), −23.84 (s, 2 B), −3.59 (d, 2 B), 2.08 (d, 2 B).

Preparation of $K_4B_{20}H_{18}$ (K_4a^2).[2] To a solution of e^2 (1.5 g, 3.5 mmol) in 30 mL of H_2O was added 12 mL of 1 N HCl. The solution was heated to 70 °C for 5 min and cooled to room temperature, and the pH was raised to 10 by the addition of KOH pellets. Recrystallization in an ice bath gave the product (1.2 g, 2.7 mmol) in 78% yield. IR (KBr): 3598 (s), 3509 (s), 2419 (s), 1613 (s), 1025 (s) cm^{-1}. ^{11}B NMR (H_2O): −29.32 (d, 8 B), −28.70 (d, 8 B), −6.14 (d, 2 B), 11.19 (s, 2 B).

General Collection and Reduction of X-ray Data. All data were collected at 25 °C in the θ–2θ scan mode. Data were corrected for Lorentz, polarization, and absorption effects. Atoms were located by use of direct methods. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis and Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSCOR, an absorption correction based on a ψ-scan; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculations based on crystal size, shape, and orientation; SHELX86 (Sheldrick), structure solution package; SHELX76 (Sheldrick), crystal structure package; MULTAN80 (Main et al.), direct methods; ORTEP (Johnson), structure plotting. All calculations were performed on the VAX 11/750 computer in the J. D. McCullough Crystallographic Laboratory. Scattering factors for H were obtained from Stewart et al.[5] and for other atoms were taken from ref 6. Anomalous dispersion terms were applied to the scattering of K. Final positional and thermal parameters are given in the supplementary materials.

Collection and Reduction of X-ray Data for $K_4B_{20}H_{18} \cdot 2H_2O$ (K_4e^2). A colorless needle, obtained from a water/ethanol solution, was mounted on a thin glass fiber on a Syntex $P\bar{1}$ diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and for $h0l$ reflections for which $l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 24 accurately centered reflections ($19.7 < 2\theta < 40.3°$). Three intense reflections (3,2,1, 0,3,−3, 1,−3,−3) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated ca. ±6%, during the course of the experiment. Of the 4109 unique reflections measured, 3562 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. An absorption correction based on ψ scans was applied.

Solution and Refinement of the Structure of $K_4B_{20}H_{18} \cdot 2H_2O$ (K_4e^2). Anisotropic temperature factors were refined for all non-hydrogen atoms. With the exception of one unlocated water hydrogen, all H atoms were included in calculated positions in structure factor calculations with an assigned u value of 0.10 or 0.04 Å^2 for water and non-water H, respectively. H parameters were not refined. Peak maxima and minima on a final difference electron density map were 0.5 e Å^{-3}.

Collection and Reduction of X-ray Data for $K_4B_{20}H_{18} \cdot 4H_2O$ (K_4a^2). A colorless parallelepiped, obtained from a water/ethanol solution, was mounted on a thin glass fiber on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 34 accurately centered reflections ($9.8 < 2\theta < 20.2°$). Three intense reflections (0,2,3, 2,2,−2, 0,2,−2) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated ca. ±5%, during the course of the experiment. Of the 3239 unique reflections measured, 2534 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. An absorption correction based on the crystal shape, size, and orientation was applied.

Solution and Refinement of the Structure of $K_4B_{20}H_{18} \cdot 4H_2O$ (K_4a^2). All H were included in calculated positions in structure factor calculations with an assigned u value of 0.04 or 0.08 and 0.15 Å^2 for anion and water H, respectively. H parameters were not refined. Anisotropic temperature parameters were refined for all non-hydrogen atoms. Maxima and minima on a final difference electron density map were 0.8 e Å^{-3}.

Collection and Reduction of X-ray Data for $K_4B_{20}H_{18} \cdot 2H_2O$ (K_4a^2). A colorless crystal, obtained from a H_2O/EtOH solution, was mounted on a fiber on the Syntex $P\bar{1}$ diffractometer described above. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and for $h0l$ reflections for which $l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 11 accurately centered reflections ($19.5 < 2\theta < 40.0°$). Three intense reflections (2,4,0, 0,3,2, 1,−1,3) were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 3% with maximum fluctuation of ±3% during the course of the experiment (21.2 h). Of the 1060 unique reflections measured, 957 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. An absorption correction based on crystal size, shape, and orientation was used.

Solution and Refinement of the Structure of $K_4B_{20}H_{18} \cdot 2H_2O$ (K_4a^2). H atoms of the water molecule were not located. All other H were kept in located positions and were assigned B values of 3.0 Å^{-2}. The largest peaks on a final difference electron density map were 0.4 e Å^{-3}.

Solid-State Structures of e^2 and a^2. Crystallographic data and selected bond distances and angles are reported in Tables I–III.

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(1) Hawthorne, M. F.; Pilling, R. L.; Stokely, P. F.; Garret, P. M. *J. Am. Chem. Soc.* **1963**, *85*, 3704.

(2) Hawthorne, M. F.; Pilling, R. L.; Stokely, P. F. *J. Am. Chem. Soc.* **1965**, *87*, 1893.

(3) Chamberland, B. L.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1450.

(4) Kaczmarczyk, A.; Dobrott, R. D.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 729.

(5) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(6) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

0020-1669/92/1331-3669$03.00/0

Table I. Crystallographic Data Collection for $K_4e^2{\cdot}2H_2O$, $K_4a^2{\cdot}4H_2O$, and $K_4a^2{\cdot}2H_2O$[a]

	$K_4e^2{\cdot}2H_2O$	$K_4a^2{\cdot}4H_2O$	$K_4a^2{\cdot}2H_2O$
formula	$K_4B_{20}H_{22}O_2$	$K_4B_{20}H_{26}O_4$	$K_4B_{20}H_{22}O_2$
fw	426.76	462.80	426.76
temp/K	298	298	298
wavelength/Å	1.5418	0.7107	1.5418
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	14.598 (1)	6.9292 (4)	6.884 (1)
b/Å	19.803 (2)	7.7204 (5)	13.242 (3)
c/Å	15.385 (1)	10.9554 (6)	11.445 (3)
α/deg		106.540 (1)	
β/deg	116.148 (2)	90.438 (2)	82.612 (7)
γ/deg		97.816 (2)	
V/Å	4010	557	1036
Z	8	1	2
ρ(calc)/gcm^{-3}	1.42	1.38	1.37
μ/cm^{-1}	80	8	77.1
R	0.065	0.052	0.056
R_w	0.118	0.073	0.091
GOF	4.60	2.45	3.75

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_0 - N_\nu)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for the $K_4e^2{\cdot}2H_2O$ Isomer

B1–B2	1.683 (13)	B2–B6	1.853 (12)
B1–B3	1.691 (12)	B2–B9	1.859 (12)
B1–B4	1.723 (14)	B4–B8	1.755 (14)
B1–B5	1.709 (13)	B7–B8	1.817 (13)
B2–B3	1.829 (12)	B10–B8	1.706 (13)
B2–B1–B3	65.6 (5)	B7–B10–B8	65.3 (6)
B5–B1–B3	99.7 (6)	B7–B10–B9	100.7 (7)
B2–B3–B4	91.0 (6)	B10–B6–B3	109.6 (6)
B6–B7–B8	90.9 (6)	B10–B8–B4	113.0 (7)
B9–B6–B7	86.6 (5)	B1–B2–B6	112.2 (6)

Table III. Selected Interatomic Distances (Å) and Angles (deg) for the $K_4a^2{\cdot}4H_2O$ and $K_4a^2{\cdot}2H_2O$ Isomers

	$K_4a^2{\cdot}4H_2O$	$K_4a^2{\cdot}2H_2O$
B10–B10	1.699 (4)	1.666 (12)
B10–B06	1.718 (3)	1.717 (9)
B10–B07	1.725 (3)	1.719 (9)
B10–B08	1.727 (3)	1.711 (9)
B10–B09	1.720 (3)	1.736 (9)
B08–B04	1.822 (3)	1.806 (8)
B01–B04	1.701 (3)	1.684 (9)
B07–B08	1.820 (3)	1.819 (9)
B03–B04	1.845 (3)	1.816 (8)
B10–B10–B08	131.3 (2)	131.22 (60)
B08–B10–B07	63.6 (1)	64.02 (36)
B08–B10–B06	96.7 (1)	95.97 (41)
B04–B01–B03	65.7 (1)	64.88 (38)
B04–B01–B02	99.3 (2)	98.57 (45)
B07–B08–B09	90.3 (1)	89.41 (40)
B03–B04–B05	89.8 (1)	89.87 (40)
B01–B04–B08	112.1 (2)	112.75 (86)
B10–B08–B04	114.0 (2)	114.40 (43)

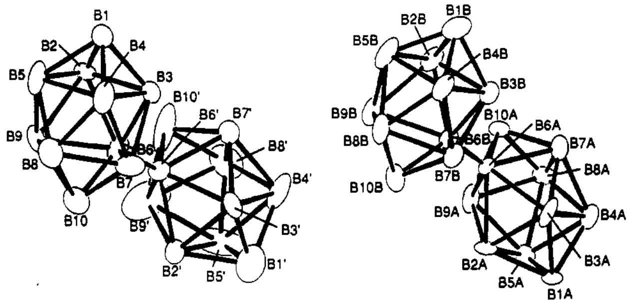
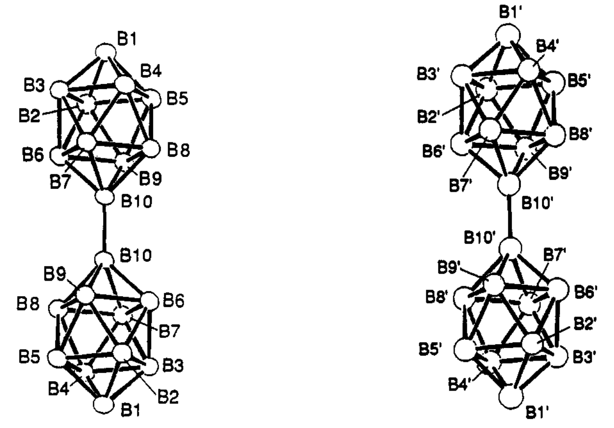


Figure 1. The e^2 anion (two crystallographically unrelated anions), showing atomic labeling. Hydrogen atoms have been omitted for clarity.



$K_4{\cdot}a^2{\cdot}4H_2O$ $K_4{\cdot}a^2{\cdot}2H_2O$

Figure 2. The a^2 anion in the tetrahydrate and the dihydrate, showing atomic labeling. Hydrogen atoms have been omitted for clarity. Both a^2 anions are centrosymmetric.

Results and Discussion

The structures of the $B_{20}H_{18}^{4-}$ isomers[2] have been formally described as two $B_{10}H_9^{2-}$ fragments joined by a two-center B–B bond. The two fragments conceivably may be joined through equatorial-equatorial (e^2, Figure 1), apical-apical (a^2, Figure 2), or apical–equatorial (ae) boron atoms of each $B_{10}H_9^{2-}$ cage. The previously[2] reported ^{11}B NMR (60 MHz) spectrum of the e^2 isomer consisted of two low-field doublets of area 2.1 and 2.2 and an unresolved high-field singlet of area 15.7. The two low-field doublets were assigned to apical boron atoms 1, 1′ and 10, 10′, each of which must carry a terminal hydrogen atom. The broad high-field singlet corresponds to all 16 equatorial boron atoms. A high-resolution ^{11}B NMR (160.463 MHz) spectrum of the same species consists of six peaks. The presence of two low-field doublets (apical borons) at 2.08 and −3.59 ppm is consistent with the previously reported spectrum. However, the broad high-field singlet (16 borons) formerly observed is now resolved at high field into a singlet and three doublets. The singlet at −23.84 ppm is assigned to the two equatorial intercage boron atoms which are not bonded to a hydrogen atom. The three doublets (−27.15, −28.54, and −29.51 ppm) of area 4, 4, and 6 correspond to the remaining equatorial boron atoms with the area 6 array derived from the accidental superposition of doublets of area 2 and 4.

The more symmetrical a^2 isomer exhibited four similar resonances, as previously reported.[2] These resonances comprise a low-field singlet, a low-field doublet, and two high-field doublets of area 2, 2, 8, and 8, respectively. The low-field singlet at 11.19 ppm and the low-field doublet at −6.14 ppm correspond to the substituted and unsubstituted apical boron atoms, respectively. The very large downfield shift of 11.19 ppm of the substituted apical boron atoms suggests that the B–B bond linkage between the polyhedra is the position of highest electron density. Peaks attributable to unsubstituted apical boron atoms in $B_{10}H_{10}^{2-}$ usually appear at −0.28 ppm.[7] When substituted with an electron-withdrawing group, as in $1\text{-}B_{10}H_9N_2^-$, the substituted apical boron was observed[8] at −14.27 ppm. The ^1H NMR of a^2 (360.136 MHz in DMF-d_7) showed a very broad signal (from ca. 1 to −0.2 ppm) centered at approximately 0.4 ppm. The application of ^{11}B decoupling caused this broad peak to collapse to two singlets at 0.18 and 0.40 ppm, respectively.

The molecular structure of the potassium salt of the e^2 isomer was solved via a single-crystal X-ray diffraction study. X-ray quality crystals were obtained from H_2O/EtOH. No decay of the crystal, a colorless needle, was observed after 2 weeks. The crystal contains two independent e^2 anions and each anion is composed of two $B_{10}H_9^{2-}$ fragments joined by a two-center boron–

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(7) Hawthorne, M. F.; Olsen, F. P. *J. Am. Chem. Soc.* **1965**, *87*, 2366.

(8) Ng, L. L.; Ng, B. K.; Shelly, K. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 4278.

boron bond through one equatorial boron atom from each cage. Each e^2 anion exists as a dihydrate and Figure 1 illustrates the two independent e^2 anions. Selected interatomic distances and angles for the salt are tabulated in Table II.

Single crystal X-ray diffraction studies of the potassium salt of the a^2 anion prove that the $B_{20}H_{18}^{4-}$ unit is composed of two equivalent $B_{10}H_9^{2-}$ cages linked together by a single bond generated from an apical boron atom contributed from each cage. The salt exists as the dihydrate and as the tetrahydrate. Both complexes are colorless crystals. However, there are no apparent differences in the a^2 anion in the two hydrates. Figure 2 illustrates the molecular structure of the a^2 isomers in both hydrates. Selected interatomic distances and angles of the salt are given in Table III. The a^2 isomer has approximate D_{4h} symmetry and is centrosymmetric. The geometry of the a^2 isomer is of interest in that the boron atoms of the equatorial belts of each cage are eclipsed with respect to the boron atoms of the corresponding belt of the opposite cage. For example, the dihedral angle B06–B10–B10′–B08′ is only 0.1° in the tetrahydrate complex. This same angle is 1.9° for the dihydrate complex. The fact that B06–B07–B08–B09 eclipses B06′–B07′–B08′–B09′ may maximize intercage electron delocalization. The bond formed between the two $B_{10}H_9^{2-}$ cages is very nearly coincident with the centerlines of the two cages. For example, the angle formed by B1–B10–B10′ is 179.6°.

The bond distances for the e^2 and a^2 isomers are all on the order of those normally found for B–B bonds.[9] The distances between equatorial (e–e) boron atoms were generally longer than distances between apical and equatorial borons (a–e), as would be expected for bonds originating from vertices having a higher coordination number.[10] The average equatorial–equatorial intercage boron (B6–B6′) bond in the e^2 isomer is 1.71 ± 0.12 Å while the average apical-apical intercage boron (B10–B10) bond in the a^2 isomer is slightly shorter, 1.68 ± 0.02 Å.

Interatomic distances in the e^2 isomer are varied and range from 1.59 to 1.91 Å overall. Apical–equatorial and equatorial–equatorial bonds vary between 1.59–1.74 Å and 1.71–1.91 Å, respectively. Bonds involving the substituted equatorial boron atom are not significantly different from bonds involving other equatorial boron atoms. The average apical (B10) to substituted equatorial boron atom (B6) distance is 1.72 ± 0.14 Å. Selected interatomic distances for one polyhedron of one e^2 anion isomer are listed in Table II. Interatomic distances for the second polyhedron of the anion and for the second e^2 isomer are similar to, and do not vary appreciably from, those tabulated.

Bond distances found for the a^2 anion are all very uniform in length, with all e–e bond distances approximately 1.82 Å. The a–e bonds furthest removed from the apical–apical (a–a) bond are all near 1.70 Å, slightly shorter than the a–e bond lengths adjacent to the a–a bond, which are on the order of 1.72 Å. The intercage a–a bond distance is essentially the same as the corresponding a–e bond distances. This consistency in bond length compares favorably with the uniformity observed in the case of unsubstituted[9] $B_{10}H_{10}^{2-}$. Table III contains selected interatomic distances for both hydrates of the a^2 isomers.

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Supplementary Material Available: A table giving details of the crystallographic data collection and tables of atom coordinates, bond distances and angles, and anisotropic thermal parameters (42 pages). Ordering information is given on any current masthead page.

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[9] Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin, Inc.: New York, 1963.

[10] Hart, H. V.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1967**, *89*, 4220.